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Photocatalytic Production of Organic Compounds from CO and H_2O in a Simulated Martian Atmosphere

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ABSTRACT **[^{14}C]CO_2 and [^{14}C]organic compounds are formed when a mixture of [^{14}C]CO and water vapor diluted in [^{12}C]CO_2 or N_2 is irradiated with ultraviolet light in the presence of soil or pulverized vycor substratum. The [^{14}C]CO_2 is recoverable from the gas phase, the [^{14}C]organic products from the substratum. Three organic products have been tentatively identified as formaldehyde, acetaldehyde, and glycolic acid. The relative yields of [^{14}C]CO_2 and [^{14}C]organics are wavelength- and surface-dependent. Conversion of CO to CO_2 occurs primarily at wavelengths shorter than 2000 Å, apparently involves the photolysis of water, and is inhibited by increasing amounts of vycor substratum. Organic formation occurs over a broad spectral range below 3000 Å and increases with increasing amounts of substratum. It is suggested that organic synthesis results from adsorption of CO and H_2O on surfaces, with excitation of one or both molecules occurring at wavelengths longer than those absorbed by the free gases. This process may occur on Mars and may have been important on the primitive earth.**

Current ideas regarding the abiogenic synthesis of organic compounds on the planets rest on the theories of Oparin (1) and Urey (2), and on the experiments of Miller (3) and others, showing that the synthesis of biologically important compounds on the primitive earth was favored by the chemically reducing character of the primitive atmosphere. The importance of an excess of a reduced gas such as hydrogen, methane, or ammonia in laboratory simulations of these processes has often been pointed out (4). In view of these findings, it appears *a priori* unlikely that a synthesis of organic matter would be demonstrable in a gas mixture compositionally similar to the oxidized atmosphere of Mars. This atmosphere consists almost entirely of CO_2 (5) with 0.1–0.3% CO (5, 6) and a small, seasonally variable quantity of water (7). Small amounts of other gases are not excluded. The mean surface pressure is about 6.5 mb (8). Solar ultraviolet (UV) reaching the surface is filtered through the CO_2, which effectively absorbs wavelengths shorter than 1950 Å. Thus, little energy is available at the surface for the activation of CO_2, CO, or water.

We have performed organic synthesis experiments with mixtures of CO_2, CO, and H_2O exposed to UV in the presence of soil or powdered vycor glass. The purpose of these tests was to uncover possible sources of error in an experiment, planned for the first Mars lander, designed to detect biosynthesis of organic matter in Martian soil (9). The findings, presented here, show that UV radiation of wavelengths above 2000 Å produces organic compounds in the substratum.

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METHODS

[^{14}C]CO was obtained, in 0.5 mCi breakseal ampoules, from Amersham/Searle. This CO had been prepared by the reduction of CO_2 over zinc at 400°C, and the unchanged CO_2 had been removed at −196°C. Several ampoules from two batches were used. Batch 19, specific activity 30.5 Ci/mol, had a specified chemical purity of 98% (less than 1% of the impurity was H_2). Batch 20 had a specific activity of 35.0 Ci/mol, with a specified radiochemical purity of 99%, and H_2 was not detected. Both batches contained some [^{14}C]-CO_2. The initial concentrations of [^{14}C]CO_2 present are indicated in the unirradiated controls.

The [^{14}C]CO ampoules were sealed to 600-ml pyrex reservoirs. The reservoirs were flushed with diluent gas, either high-purity [^{12}C]CO_2 or N_2, then evacuated and the breakseals were ruptured to permit expansion of [^{14}C]CO into the reservoirs. The reservoirs were then brought to a total pressure of 1 atm by filling with diluent gas and with about 50 ml of liquid water previously flushed with the diluent gas. The [^{14}C]CO reservoirs were attached to a pyrex manifold which had five positions for attachment of sample chambers. The latter consisted of quartz tubes (1.3 × 8 cm) with a detachable pyrex section containing a stopcock. Each chamber had a gas volume of about 5.5 ml. The chambers were evacuated and flushed with diluent gas, then filled manometrically to 1 atm with [^{14}C]CO and diluent gases. The pressure in the reservoir was maintained at 1 atm by adding water flushed with diluent gas.

The vacuum system contained a liquid nitrogen trap to prevent diffusion of impurities from the mechanical vacuum pump. The vacuum indicator was a Wallace and Tiernan Gage. The gas reservoirs, manifold, and sample chambers were constructed of new glass that presumably had never been exposed to mercury. Also, all glassware was cleaned with 8 N HNO_3 to minimize adventitious mercury contamination.

The organic soil was an arable, fertile, brown soil with particle size less than 1 mm. Before exposure to [^{14}C]CO, the soil was sterilized overnight in an oven at 175°C and then equilibrated for 1 hr at 100% relative humidity at 23°C. The vycor substratum was 80–100 mesh, highly fractured particles with a surface area of 173 m^2/g. Before use, the vycor was heated to 720°C in air and equilibrated with water vapor as described above.

Sample chambers containing gas mixtures were irradiated in a horizontal position with the soil or vycor substratum spread over the quartz portion of the chamber. The source of UV was either a 150-watt high pressure xenon lamp (Hanovia No. 901C1) or a low-pressure mercury lamp (Pen-Ray No. SCT-1). The total intensities of radiation (UV and visible)

reaching the chambers were 30 and 1 mW/cm² for the xenon and mercury lamps, respectively.

Lamp intensities were measured using calibrated Eppley thermopiles. The energy emission spectrum of the xenon lamp was calculated from relative intensity spectra taken on a McPherson 225, 1-m vacuum monochromator, and the absolute energy emitted by the lamp over a portion of the spectrum isolated by an interference filter. Absorption spectra were measured with a Cary-14 recording spectrophotometer.

The levels of ^{14}C in CO and CO_2 were determined by two methods that gave comparable results. In the first method, the gas phase from the sample chamber was fractionated in a gas chromatographic column packed with 60–80 mesh silica gel. The column effluent was oxidized by passage through a CuO column at 700°C. The original CO_2, and the CO_2 derived from the combustion of CO, were trapped in hyamine hydroxide (1 M in methanol) and counted as described below. The peaks of radioactivity were identical to the elution times for authentic CO and CO_2. In the second method, the gas phase was drawn into an evacuated reservoir, mixed with $[^{12}C]CO$, and then flushed through a series of bubblers containing hyamine hydroxide. The first two bubblers, which contained 1 ml of hyamine hydroxide, trapped the $[^{14}C]CO_2$. The effluent, containing over 99.5% of the $[^{14}C]CO$, was passed over hot CuO and the resulting $[^{14}C]CO_2$ was trapped in 3 ml of hyamine hydroxide.

The $[^{14}C]$organics were extracted by rinsing the substratum from the sample chamber with 5 ml of water, and then heating the water and the substratum for 5 min at 100°C. In all cases, unirradiated control samples were carried through the work-up and counting procedures.

All measurements of radioactivity were made in a liquid scintillation counter (Beckman LS-100) with a counting efficiency of 57%. All data are corrected for background radioactivity, which was 14 cpm. The $[^{14}C]CO_2$ in hyamine hydroxide was counted in toluene with 0.5% (w/v) of 2,5-diphenyloxazole (PPO). Aqueous extracts were counted in dioxane with 10% (w/v) naphthalene and 0.5% (w/v) PPO.

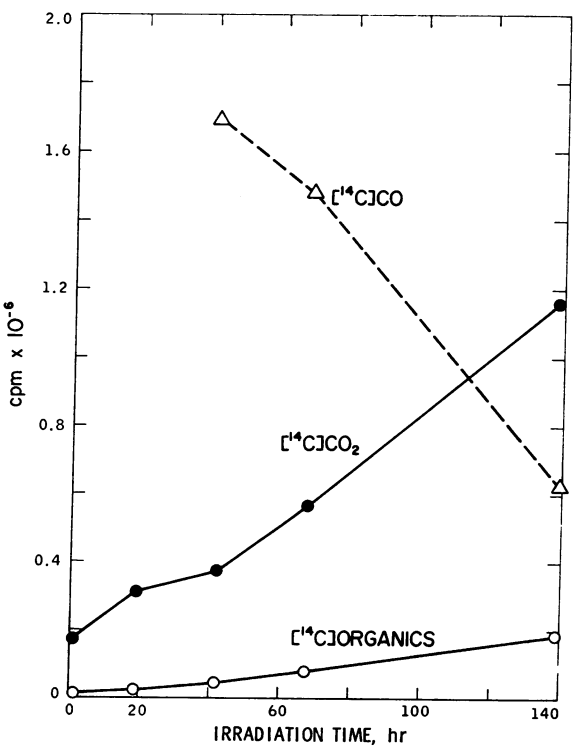

FIG. 1. Production of CO_2 and organics by xenon irradiation of sample chambers containing 30 mg of sterilized soil, 97% CO_2, 2.8% H_2O vapor, and 0.37% CO ($^{12}C + ^{14}C$).

TABLE 1. *Production of CO_2 and organics by UV irradiation of different concentrations of CO*

CO %	% Conversion* of CO to		Relative production rates	
	CO_2	Organics	CO_2	Organics
0.02	48.7	5.1	0.4	0.042
0.37	5.0†	1.15†	0.76	0.18
5.5	0.44‡	0.12‡	1.0	0.27

Quartz chambers contained 30 mg of sterilized soil in a gaseous mixture of the indicated CO concentration, 2.8% water vapor, and the balance CO_2.

* Based on the yields of $[^{14}C]CO_2$ and $[^{14}C]$organics after 17 hr of irradiation with a xenon lamp.

† Calculated from Fig. 1.

‡ Calculated from determinations made after irradiation for 135 and 216 hr.

For identification of unknowns, samples of substratum were extracted with 0.1 N NH_4OH for 5 min at 100°C. The extracts were concentrated under a stream of N_2 and applied to thin-layer chromatograms. Tentative identifications were made by comparing the R_f values of unknown and authentic ^{14}C-labeled compounds on radioautograms prepared from the thin-layer chromatograms. Further identification was made by treating the ^{14}C-labeled unknowns with $LiAlH_4$ in diethyl ether. The reduced products were mixed with known $[^{12}C]$-alcohols and analyzed for ^{14}C by gas chromatography on Poropak Q and Carbowax 20 M-Chromosorb W columns.

RESULTS

When quartz chambers containing sterilized soil and a mixture of $[^{14}C]CO$, $[^{12}C]CO_2$, and water vapor were irradiated with the xenon lamp, the $[^{14}C]CO$ was converted to $[^{14}C]CO_2$, recoverable from the gas phase, and to organic compounds, recoverable from the soil substratum (Fig. 1). Both reactions proceeded linearly with time until $^2/_3$ of the CO was consumed (138 hr). Other experiments showed that the net rate of formation of organics was much slower after more than 95% of the CO had been converted to organics and CO_2, and in some cases there was net breakdown at this point. This indicates that ^{14}C from CO was converted to organics without first being oxidized to CO_2. As shown below, the conversion represents *de novo* synthesis from $[^{14}C]CO$ rather than an exchange or addition into organic matter present in the soil.

The gas phase of irradiated samples did not contain appreciable levels of ^{14}C-labeled compounds other than CO or CO_2. More than 99.9% of the ^{14}C in the gas phase readily passed through a 50-cm firebrick-CuO column at 120°C. Only highly volatile carbon compounds such as CO, CO_2, and CH_4 are eluted at this temperature (9). Also, only CO_2 and CO were detected by low-resolution mass spectrometric analysis of the gas phase of an irradiated chamber containing $[^{13}C]CO$, $[^{12}C]CO_2$, water vapor, and ignited soil (unpublished data).

The rate of conversion of CO to CO_2 did not increase proportionally when the initial concentration of CO was in-

TABLE 2. *Role of the substratum in the UV-dependent conversion of CO to CO_2 and organics*

Vycor substratum (mg)	Xenon UV (hr)	Radioactivity* in ^{14}CO	Radioactivity* in $^{14}CO_2$	Radioactivity* in [^{14}C]-organics	% of total ^{14}C in CO_2	% of total ^{14}C in organics
30	none	60.5	1.47	0.0005	2.4	0.001
none	17	3.76	45.0	0.91	90.7	1.84
none	69	1.41	47.8	0.21	96.8	0.44
30	17	25.0	27.8	1.72	51.1	3.15
150	17	40.1	10.8	1.28	20.7	2.46
150	69	19.6	33.0	3.42	59.0	6.1
500	163	8.1	32.3	5.33	70.6	11.7

Quartz chambers contained the indicated quantity of powdered vycor and a gaseous mixture of 0.06% [^{14}C]CO, 2.8% water vapor, and 97% [^{12}C]CO_2.

* Expressed as cpm $\times 10^{-5}$.

creased (Table 1). In 17 hr of irradiation, a 275-fold increase in CO concentration gave only a 2.5-fold increase in CO_2 production. The yield of organics was increased by 6.4-fold. The fact that both processes increased only slightly with increasing CO concentration implies that some component other than CO was limiting. As will be shown, organic production is reduced when insufficient amounts of substrata are present. Also, a deficiency of water limits both organic and CO_2 production.

When the quartz chamber contained no added substratum, 17 hr of irradiation converted 90% of the [^{14}C]CO to [^{14}C]CO_2 and 1.8% of the [^{14}C]CO to organics, which were extractable from the walls of the chamber (Table 2). A longer irradiation time gave a greater conversion from CO to CO_2 and the organic yield was reduced accordingly. With the inclusion of ignited vycor powder, the conversion of CO to CO_2 was diminished, and a greater proportion of the CO consumed was converted to organics. Evidently the organics accumulate on surfaces.

The conversion of CO to organics occurs when N_2 is substituted for CO_2 as the major constituent in the gas mixture (Table 3). The conversion of [^{14}C]CO to [^{14}C]CO_2 at comparable rates with N_2 or [^{12}C]CO_2 as diluent gas negates the possibility that this conversion occurs via exchange of the label into the pool of unlabeled CO_2.

TABLE 3. *UV-dependent conversion of CO to CO_2 and organics in various gas mixtures*

Diluent gas*	Vycor* substratum (mg)	Xenon UV (hr)	% Conversion of [^{14}C]CO to (*A*) [^{14}C]CO_2†	% Conversion of [^{14}C]CO to (*B*) [^{14}C]-organics	*A*/*B*
97% N_2	none	17	77.6	0.91	85.2
	30	17	51.0	1.05	48.5
	150	17	10.6	1.14	9.3
97% [^{12}C]CO_2 + 0.03% O_2	none	17	89.0	1.14	78.0
	30	17	34.6	2.12	16.3
	150	69	82.0	2.46	33.5

* Chambers contained 0.06% [^{14}C]CO, 2.8% H_2O vapor, and the indicated additions.

† Corrected for the concentration of $^{14}CO_2$ present in unirradiated controls.

TABLE 4. *Conversion of CO to CO_2 and organics by irradiation with UV sources of different spectral quality*

UV Source	Filter	% Conversion of [^{14}C]CO to (*A*) [^{14}C]CO_2*	% Conversion of [^{14}C]CO to (*B*) [^{14}C]organics	*A*/*B*
Xenon	air†	47.7	1.55	30.8
	water†	1.9	0.36	5.3
	methanol†	<0.4	0.096	<4.4
	pyrex‡	<0.1	0.016	...
Low-pressure mercury	air†	36.1	1.03	35.0
	water†	<0.6	0.72	<0.9
	methanol†	<0.4	0.48	<0.9
	pyrex‡	<0.1	<0.002	...

Quartz chambers containing 30 mg of vycor and a gaseous mixture of 0.06% [^{14}C]CO, 2.8% H_2O vapor, and 97% [^{12}C]CO_2 were irradiated for 17 hr.

* Corrected for the 2.4% [^{14}C]CO_2 present in unirradiated controls.

† Quartz cell with 5-cm light path.

‡ 4-mm plate.

The presence of O_2 did not significantly affect the conversion of CO to CO_2 and organics (Table 3). Although the concentration of oxygen in the Martian atmosphere is not known, our mixture of 0.06% CO and 0.03% O_2 was used as a simulation of proportions present in the lower atmosphere on the assumption that CO and O are produced from UV photolysis of CO_2 and there is no oxygen sink. Other studies showed that argon, a possible component of the Martian atmosphere, did not affect the conversion of CO to CO_2 or organics.

Other experiments showed that reducing the concentration of water vapor caused a marked reduction in the rates of conversion of CO to CO_2 and organics. For example, when the N_2 flush and diluent gas were dried by passage through a liquid-N_2 trap, and the vycor substratum was exposed only to ambient water vapor, the yields of [^{14}C]CO_2 and [^{14}C]organics were 11 and 5%, respectively, of those observed in experiments with more water present. Limiting water also reduced both conversions when [^{12}C]CO_2 was the diluent gas. Although the amounts of water in the gas phase and on the surfaces are not precisely known, our findings implicate water as a reactant in both conversions.

The rates of the two reactions can be lowered by reducing the intensity of the shorter wavelengths of UV radiation by passage through filters (Table 4). Filtration through 5 cm of liquid water or methanol caused a greater percentage inhibition of the CO to CO_2 conversion than of the CO to organics conversion. CO_2 production was abolished when the xenon UV was filtered through pyrex, but a small amount of ^{14}C was detected in the aqueous extract of the vycor substratum. Both reactions were completely inhibited when the mercury UV was filtered through pyrex.

The absorption spectra of the filters and the emission spectra of the UV sources are shown in Fig. 2. The inhibition of CO_2 formation with the water filter (Table 4) indicates that this process occurs primarily with UV wavelengths shorter

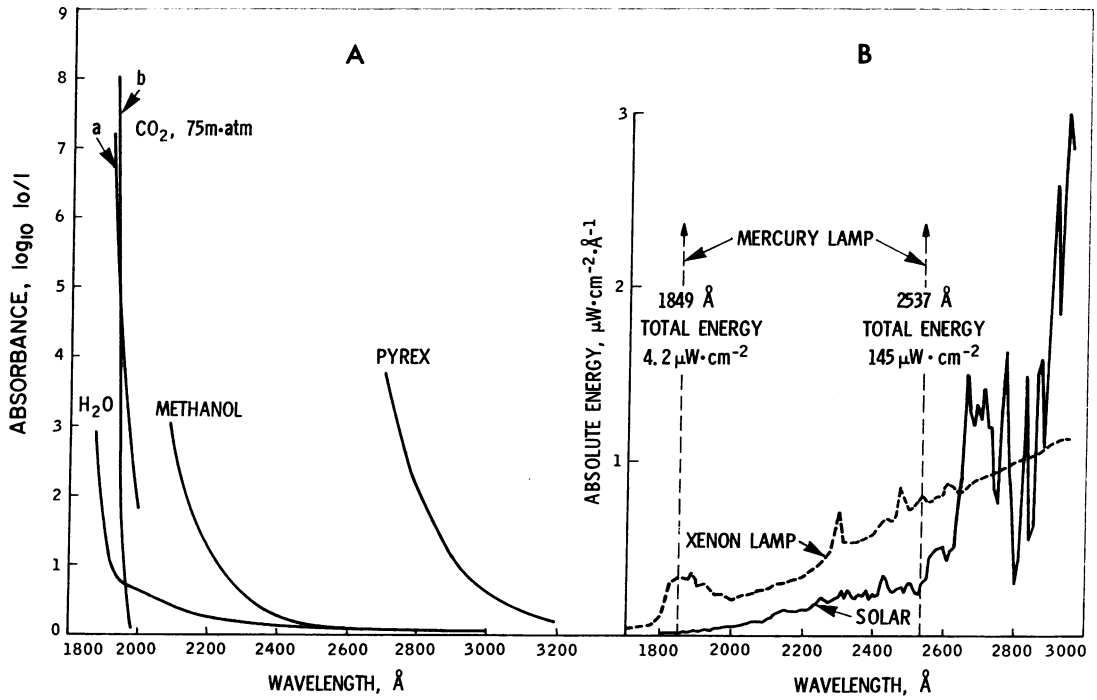

FIG. 2. (*A*). UV absorption by the concentration of CO_2 in Martian atmosphere, 5 cm of liquid H_2O, 5 cm of methanol, and 4 mm of pyrex. The absorbance of 75 m-atm of CO_2 was calculated from absorption coefficients: *a* = partially extrapolated data of Thompson *et al.* (10); *b* = unpublished values measured by A. L. Lane.

(*B*) Solar UV spectrum reaching the outer atmosphere of Mars, and the UV emission spectra of the xenon and mercury lamps. The solar spectrum was calculated from the data of McAllister (11).

than 2000 Å. When the xenon UV was filtered through methanol, the yield of CO_2 was about $1/5$ of that observed when the water filter was used. Little difference was observed in CO_2 production with the mercury source filtered through water or methanol, thereby implicating the 1849-Å Hg line as the active part of the spectrum.

The active spectrum for the conversion of CO to organics is more difficult to define. The 2537-Å line of the mercury lamp is implicated, since the water and methanol filters, which absorb 99% of the radiation below 1890 and 2130 Å, respectively, only partially inhibited the reaction. However, the xenon source, filtered through water or methanol, gave organic yields that were $1/5$ or $1/16$ of the unfiltered control. It would appear that radiation over a broad range below 3000 Å can cause organic formation.

The xenon lamp gives a good approximation of the UV radiation reaching the outer atmosphere of Mars (Fig. 2*B*). Since the conversion of CO both to CO_2 and to organics is dependent on water, which is confined to the lower atmosphere of Mars (7), and since surface catalysis appears to play an important role in the conversion to organics, our concern is with the UV spectrum that reaches the Martian surface. The major absorber in the Martian atmosphere is atmospheric CO_2, which provides a UV filter intermediate between water and methanol (Fig. 2*A*). Thus, a good approximation to the relative reaction rates for CO_2 and organic production at the Martian surface would be a value intermediate between those observed with the xenon lamp filtered through water and through methanol.

Other experiments have shown that when the unfiltered xenon lamp is used, organics collect on vycor and soil even when the substrata are shielded from direct illumination. When the lamp was filtered through water or methanol, however, organics were barely detectable on shielded substrata. Apparently the gases can be activated directly to form organic compounds by short wavelengths, but at wavelengths greater than 2000 Å, activation occurs only on surfaces.

The extracts of irradiated organic soil showed four major ^{14}C-labeled spots on radioautograms prepared from thin layer chromatograms. One unknown (1) and glycolic acid had identical R_f values under all conditions tested, namely, on silica gel or cellulose plates developed in four solvent systems. Another unknown (2) behaved identically with formaldehyde and acetaldehyde (unresolved) in three alkaline solvent systems. However, in an acid solvent, neither of the aldehydes nor the unknown (2) was detected, probably because they evaporated during chromatography. The other two unknowns were not identified. These same four ^{14}C-labeled spots were detected under every condition examined, namely, on sterilized soil, ignited soil, or vycor, with mercury or xenon irradiation, and with N_2 or $[^{12}C]CO_2$ as the diluent gas. However, the quantity of unknown (1) (glycolic acid) was lower when vycor was the substratum.

After reduction of the NH_4OH extract of irradiated sterilized soil with $LiAlH_4$, the ^{14}C-labeled compounds detected were methanol, ethanol, 1-propanol, and 1,2-ethanediol in a ratio of 46:8:4:3, respectively. Presumably, the methanol, ethanol, and ethanediol were formed, at least in part, from the reduction of formaldehyde, acetaldehyde, and glycolic acid. The compound giving propanol after reduction was not identified on the thin-layer chromatograms.

Considerable attention was given to the possibility of contaminating materials acting as photosensitizers for organic production. Mercury vapor did not appear to be such a con-

taminant. As described in *Methods*, considerable care was exercised to prevent its introduction. In addition, placing gold-plated silver wool in the reaction chambers to remove Hg vapor did not reduce organic production. One possible sensitizer considered was the Apiezon N lubricant used on the stopcocks of the chambers. However, shielding the greased area from direct irradiation did not affect organic production.

DISCUSSION

Of the two reactions we have studied, the oxidation of CO to CO_2 is almost certainly brought about by OH radicals produced in the photolysis of water vapor at the shorter wavelengths. This reaction is well known and amply documented (12). It is inhibited at surfaces (12), as we observed (Table 2).

The synthesis of formaldehyde and other organics might be accounted for by H atoms arising from water photolysis. If gas-phase photolysis were the whole story, however, we would expect the CO_2:organic ratio to remain reasonably constant over the wavelength range studied. Examination of Table 4 shows that this ratio is strongly wavelength-dependent; more CO_2 is produced at shorter wavelengths.

A plausible explanation of the organic synthesis at long wavelengths can be found in the observation of Terenin (13) that water and ammonia adsorbed on silicates are photodissociated at wavelengths longer than those at which the gases absorb. Terenin suggested that this finding could account for the puzzling photolysis of water and synthesis of formaldehyde from CO and H_2O reported in experiments performed with mercury lamps early in the century. A reading of these older papers makes it clear, however, that in many cases the reactions were Hg-sensitized (14), and it is doubtful if Terenin's hypothesis is necessary to explain any of the early observations. On the other hand, we believe that it is applicable to our experiments. Photolysis of silicate hydrates and release of H and OH radicals, followed by reduction of CO in the gas phase, cannot account for the wavelength dependency of the reactions since radicals discharged from the surface would be expected to be in the same electronic state as those produced in the gas phase. Rather, a surface-catalyzed reduction in which CO is also adsorbed to surfaces seems to be required. Excitation of the adsorbed CO may occur. A possibly similar phenomenon has been reported by Daubendiek (15) for isomerization of 1,3-pentadienes on pyrex surfaces at relatively long wavelengths. Further work will be required to determine if CO actually is being photoactivated.

Our findings suggest that UV presently reaching the Martian surface may be producing organic matter. The rates of production would be limited by the low partial pressures of CO and H_2O in the Martian atmosphere but the amount of product formed could be considerable over geological time. A substantial accumulation could occur only if the products are protected from ultimate destruction by UV radiation. This would require that the products be periodically buried. The dust storms that are reported to occur on Mars (16) might conceivably perform this function. If traces of ozone exist in the lower atmosphere of the planet, as has been suggested (17), some organic matter would probably be reoxidized.

Formaldehyde and acetaldehyde are important starting materials for the synthesis of several organic compounds. For example, aldehydes readily polymerize under UV (18), or in a $CaCO_3$-catalyzed reaction, to yield sugars and sugar-like materials. In addition, aldehydes are reactive with nitrogenous compounds such as HCN, NH_3, and amines. Although no form of nitrogen has been detected in the Martian atmosphere, nitrogen-containing compounds may be present in the surface material. These possibilities will have to be considered in planning experiments for the first Martian lander.

Because of the higher pressures of the reacting gases, these reactions may have been more important on the primitive earth than on Mars. It has been recognized that a major difficulty of the Oparin–Urey theory is the low concentration of products expected under the homogeneous reaction conditions often assumed for the prebiotic earth (19). A surface-catalyzed synthesis of organic matter of the kind we have described would alleviate this difficulty to a considerable degree by making available for organic syntheses the large amount of solar energy in the 2000- to 3000-Å region, by providing a mechanism for concentrating the products, and by extending the period of prebiotic organic synthesis beyond the time when the earth lost its hydrogen-rich atmosphere.

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